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(54) Title of Invention: Method of Manufacture of β-Tricalcium Phosphate Sintered Materials
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Details of the Invention

1. TITLE OF THE INVENTION
Method of Manufacturing β-Tricalcium Phosphate Sintered Materials.

2. RANGE OF CLAIMS
Method of manufacturing β-tricalcium phosphate sintered materials, wherein 1 mole of β-tricalcium phosphate (β-$3CaO \cdot P_2O_5$) and 0.02 ~ 0.15 mole of aluminum fluoride (AlF_3) are mixed to form a uniformly mixed powder, and wherein this mixed powder is molded into desired shaped and then sintered at a temperature ranging from 1200°C to 1400°C.

3. DETAILED DESCRIPTION OF THE INVENTION
As β-tricalcium phosphate (abbreviated as β-C_3P hereafter) is a promising material for synthetic bones, many studies have been done on the synthesis and sintering method of this material. However, materials having adequate mechanical strength have not been obtained. One reason is that phase transition of β-C_3P to a high temperature form of α-C_3P occurs at 1180°C. Thus, the crystal density changes from 3.07 to 2.77, which results in volume expansion and weakening of the sintered body structure. To circumvent this problem, heat treatment had been performed at below this phase transition temperature (1180°C) in conventional methods. However, as tricalcium phosphate powder does not completely sinter at a temperature below 1250°C, sintered materials produced by those conventional method showed only limited strengths. Thus the phase transition characteristic of β-tricalcium phosphate itself is the fundamental hindrance in producing its high strength sintered materials.

In this invention, studies have been performed on the effect of various inorganic additives and the adding conditions for the purpose of suppressing the phase transition of β-C_3P. As a result of the investigation, aluminum fluoride has been found to have a remarkable effect even at a trace concentration level. The detail is further discussed below.

Preparation of β-C_3P powder : β-$2CaO \cdot P_2O_5$ which is made by pre-baking calcium hydrogen phosphate ($CaHPO_4 \cdot 2H_2O$) for 5 hours at 850°C is mixed with calcium carbonate ($CaCO_3$) at a mole ratio of (1:1). The mixture is wet-blended using a pot mill or ball mill. The mixed powder, dried, heat-treated for more than 24 hours at 1050°C to obtain β-C_3P, which is wet-milled for longer than 48 hours using a pot mill or a ball mill.

To β-C_3P powder thus prepared, aluminum fluoride is added and wet-blended to form a uniform mixture. In the following, the amount of added aluminum fluoride and its effect on the phase transition of β-C_3P are discussed.

Several batches of samples were prepared by adding various amounts of aluminum fluoride in the range of 0.02 ~ 0.26 mole per 1 mole of β-C_3P. The samples were sintered at 1200 ~ 1400°C and the amount of α-C_3P (high temperature form) was determined to establish the correlation. The β - α phase transition rate (%) was defined as the ratio of α-C_3P vs. the total amount of β-C_3P + α-C_3P.

With the addition of aluminum fluoride (AlF_3) at 0.02 mole, β - α phase transition rate of the product sintered at 1200°C was at most 40%. At 1300°C and 1350°C, the transfer phase rate almost reached 80%. With addition of 0.04 moles, the phase transition rate was 0% at 1200°C. At 1300 and 1350°C, it was at most 40 ~ 45%. With the addition of increased amount of 0.06 ~ 0.08 mole, the phase transition rate was suppressed to 15 ~ 20% even at a high temperatures of 1300 and 1350°C. The results are summarized in Figure 1.

The added AlF_3 not only suppresses the phase transition of β-C_3P, but also produces fluorinated apatite by reacting with β-C_3P. With the addition of AlF_3 greater than 0.1 mole, formation of fluorinated apatite becomes dominant, drastically reducing the amount of tricalcium phosphate. From these results, the upper limit of the amount of AlF_3 to be added to β-C_3P was set at below 0.08 moles. It was also found that the increased amount of fluorinated apatite formation tends to reduce the bending strength of the sintered materials. The study showed that the optimum amount of AlF_3 to be added is in the range of 0.06 ~ 0.08 moles where suppression of phase transition is satisfactory, while a high bending strength is maintained. The results of one part of bending strength measurements, obtained at 0.06 moles of added AlF_3 followed by heating for 1 hour at the sintering temperatures are shown in Table 1.

Table 1

Sintering temperature (°C)	1200	1250	1300	1350	1400
Bending strength (kgf/cm^2)	1050	1390	2060	1610	900

Bending strength of tricalcium phosphate sintered body greater than 2000 kgf/cm^2 well surpasses the conventional levels. This was attained by suppressing the phase transition of β-C_3P crystal with the addition of as small as 0.06 ~ 0.08 moles of aluminum fluoride to enable the sintering at high temperatures of 1300 ~ 1350°C. A theory of aluminum fluoride addition affecting the β-C_3P phase transition temperature, is as follows. The heat decomposition peak temperature, according to DSC and TGA measurements, is about 1200°C. Fluorine produced by the decomposition reacts immediately with tricalcium phosphate to produce fluorinated apatite. The activated aluminum atoms, on the other hand, diffuse into β-C_3P crystal lattice to easily form s solid solution. The formation of the solid solution reduces the free energy and raises the phase transition temperature.

This type of tricalcium phosphate sintered materials are expected to find applications not only to bioceramics such as for synthetic bones, but also for the development of general industrial high strength materials.

Examples are shown below.

[Embodiment 1]

A uniformly mixed powder of 1 mole of β-C_3P synthesized according to the described above, and 0.04 moles of aluminum fluoride was press-molded into a round disk, 50 mm in diameter and 6 mm in thickness. The disk was sintered for 1 hour at 1250°C in an electric furnace, cooled in the furnace, and the obtained sintered body was tested for bending strength and analyzed for the phase composition. The results obtained were as follows;

Bending strength : 1140 kgf/cm^2
β - α phase transition rate (%) : 33%

[Embodiment 2]

A mixed powder of 1 mole of β-calcium phosphate and 0.06 moles of aluminum fluoride was press-molded into a round disk in the same manner as for Embodiment 1. The disk was sintered for 1 hour at 1250°C. The properties of this sintered body were as follows;

Bending strength : 2060 kgf/cm^2
β - α phase transition rate (%) : 26%

[Embodiment 3]

A mixed powder of 1 mole of β-tricalcium phosphate and 0.08 moles of aluminum fluoride was press-molded into a round disk in the same manner as for Embodiments 1 and 2. The disk was sintered for 1 hour at 1350°C. The properties of this sintered body were as follows;

Bending strength : 1530 kgf/cm^2

β - α phase transition rate (%) : 19%

4. BRIEF EXPLANATION OF THE FIGURE

Shown in Figure 1 is the correlation between the ratio of β-tricalcium phosphate vs. aluminum fluoride added (mole ratio) and the effect of β-tricalcium phosphate on the phase transition.

The horizontal axis is the ratio of β-tricalcium phosphate ($3CaO \cdot P_2O_5$) vs. aluminum fluoride (AlF_3) added in mole ratios. The vertical axis is the ratio of α-tricalcium phosphate vs. the total amount of β- and α- tricalcium phosphate in %.

Symbols in the figure indicate the temperatures at which the samples were sintered.

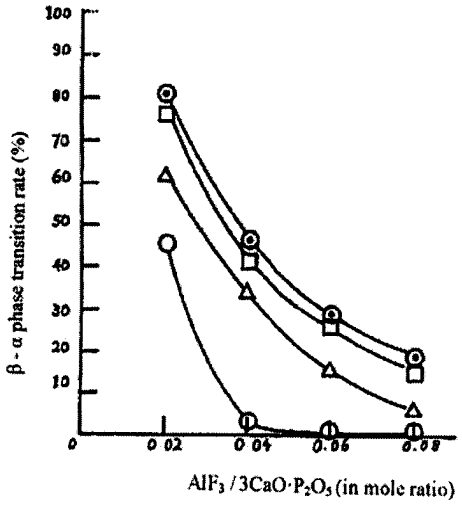
○ ..... / 1200°C

△ ..... / 1250°C

□ ..... / 1300°C

◎ ..... / 1350°C

Figure 1



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